

Charge-Transfer in Fullerene Porphyrin Ensembles

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transfer replaces electron transfer in deactivating
the photoexcited chromophore.

As far as the electron transfer chemistry of fullerenes is concerned, the most prominent donor-acceptor example implies to link one or several porphyrinic moieties, functioning as a chromophore unit and/or electron donor, to the electron accepting fullerene.

In this contribution a comprehensive series of (i) rigid, (ii) flexible and (iii) self-assembling donor-acceptor composites will be presented and compared to untangle several fundamental issues.

Firstly, the ground state of these photoactive ensembles is, whenever structurally possible, dominated by a distinguished electronic interaction. Manifest of this coupling is, besides substantial red-shifts and diminishing of the porphyrin's Soret- and Q-band transitions, the appearance of a new charge-transfer transition located in the near-infrared region. *Via* altering the spatial distance and orientation between the donor and acceptor moiety the intensity of this transition could be correlated to the electronic overlap.

Secondly, charge separation and charge recombination dynamics were probed in increasingly polar solvents, ranging from non-polar toluene all the way to the strongly polar dimethylformamide. In light of charge-recombination kinetics, the overall most important feature is that the lifetime of the radical pair is governed by the associated thermodynamics. As a consequence, intramolecular rates in (i) the rigid and (ii) the flexible dyads are clearly shifted into the inverted region of the Marcus parabola, where the electron transfer rates decrease with increasing driving forces. At first glance, this observation corroborates those seen for several rigid-spaced donor-acceptor couples (*i.e.*, zinc porphyrin / fullerene). However, in the case of flexibly spaced dyads it suggests that the fullerene and porphyrin moieties are held in close proximity to each other, even when the structure of the spacer does not enforce such an alignment. This peculiar effect is driven in large by strong π - π associations as they prevail between the π -system of the donor and acceptor.

Thirdly, spectroscopic and photochemical evidence will be presented for complexation of DABCO to a series of flexible triads, and thereby affording the corresponding tetrads. This constitutes a powerful means to control the design of rigidly, confined donor-acceptor systems. In polar media these readily available and stable ensembles are subject to a rapid intramolecular electron transfer. Conversely, in a non-polar medium energy